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⑪ Publication number:

0 413 589 A1

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EUROPEAN PATENT APPLICATION

COPY

⑲ Application number: 90309023.1

⑤① Int. Cl. 5: **C25D 11/22**

⑳ Date of filing: 17.08.90

③① Priority: 17.08.89 MX 17234

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④③ Date of publication of application:
20.02.91 Bulletin 91/08

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⑥④ Designated Contracting States:
BE CH DE ES FR GB LI NL SE

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⑤④ Improved electrolytic method for colouring anodized aluminium.

⑤⑦ The invention provides an improved electrolytic process for producing anodized metal substrates such as aluminum or aluminum alloys colored using optical interference effects. In particular, the invention pertains to a novel electrolytic method of modifying the anodic barrier layer. The method results in all colors of the visible spectrum without the need for anodizing in a separate phosphoric acid-based electrolyte.

The modification procedures consists of treating the metal substrate with a sequence of direct and alternating currents. The alternating current is symmetrical, the voltage of the positive half-wave equal to that of the negative half-wave. A preferred sequence is direct current, alternating current, direct current. As a result, metallic oxide is deposited within the enlarged pores to a defined height, thus achieving the decomposition of light and obtaining the different colors of the visible spectrum. The modification step can be performed in the anodizing bath, the electrocoloring bath, or in specific bath with an acid electrolyte.

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increased brightness of colors. The use of a defined sequence of direct and alternating current to modify the pores of the anodic aluminum oxide film and barrier film is designed to more precisely control the dimensions of said films without the need for a second anodizing bath of phosphoric acid. The improved method uses inexpensive and easily obtained equipment.

5 In one aspect of the invention, a process for the electrolytic coloring of metallic substrate is provided by the following steps:

- (a) developing a porous anodic film on the substrate in a sulphuric acid electrolytic bath;
- (b) modifying the anodic barrier film by sequentially applying to the substrate a series of voltages; a first voltage of direct current, a second voltage of alternating current, and, optionally, a third voltage of direct

10 current;

- (c) electrolytically depositing an amount of inorganic material in the pores previously modified in step (b).

In a preferred embodiment, the alternating current used in the modifying method is symmetrical so that the peak voltage of the positive half-wave is equal to the peak voltage of the negative half-wave. The final direct current application is designed to redissolve any electrolytically-deposited inorganic material and to

15 insure uniformity of the barrier film.

In another aspect of this invention, the modification step as outlined above can be performed in either the sulphuric acid anodizing bath, in a separate modification bath, or preferably, in the electrocoloring bath itself.

In a further aspect of this invention, direct current is optionally applied to the metal substrate after the

20 electrocoloring step to redissolve the inorganic deposits. This procedure allows for fine scale adjustment of the color tone, resulting in more precise control of the colors of the final aluminum or other metallic product.

An aluminum article having an anodic oxide coating on its surface is also described, said article produced according to the following process:

- a. developing a porous anodic film on the substrate in a sulphuric acid electrolytic bath;
- 25 b. modifying the anodic barrier film by sequentially applying to the substrate a first voltage of direct current, a second voltage of alternating current and a third voltage of direct current;
- c. electrolytically depositing an amount of inorganic metallic material in an electrocoloring bath, a material deposited within the pores of the oxidizing layer.

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Brief Description of the Drawings

FIG. 1 is a schematic illustration of the anodic layer formed on the substrate during the anodization step.

FIG. 2 illustrates the effect of the alternating current treatment of the modification step, serving to

35 increase the diameter of the pore by forming a cavity.

FIG. 3 illustrates deposition of inorganic material in the pores of the anodic layer during the electrocoloring step.

DETAILED DESCRIPTION OF THE INVENTION

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Referring to FIGS. 1-3, the anodizing process and the improved method of the present invention are schematically illustrated. Before the metal substrate 10 is subjected to the anodizing process, it is prepared using conventional methods for achieving a uniform, smooth and attractive finish. Initial treatments can

45 comprise degreasing, matting, polishing, rinsing and neutralizing.

The prepared piece is then deposited in the anodic oxidation tank 11 which tank generally contains an acid solution comprising sulphuric acid 12. In some cases, additives can be used in the sulphuric acid bath to diminish the dissolution strength of the electrolyte. Other acids or acid mixtures such as a mixture of sulphuric acid and chromic acid can also be used in the conventional anodizing bath.

50 The substrate 10 is then subjected to an anodizing flow of direct 13 current wherein the substrate is the positive electrode (anode) and electrodes 14 made of aluminum, carbon, lead, stainless steel and the like, are the negative electrode (cathode).

In this anodizing step, if the substrate 10 is aluminum, an anodic layer 16 is formed on the substrate (FIG. 1). The layer 16 is porous, containing a plurality of evenly spaced pores 18, the distance between the

55 bottom of a pore 18 and the substrate 10, being defined as the barrier film 20. The thickness of the layer 16 and the length and depth of the pores 18 will vary depending on many variables such as time, which will determine the pore thickness; voltage, which will determine the barrier film 20 size; temperature, which will determine the diameter of the pore in addition to the dissolution rate of the anodic layer, and current

the anodizing layer so that the pore diameters, the cavity dimensions, and the barrier film thickness may not be entirely uniform. The final DC current treatment is applied for a time sufficient to adjust the thickness of the barrier film 20 to the extent necessary to form a film appropriate for the chosen color and to ensure uniformity of barrier film thickness. The uniformity of the barrier film is directly related to the uniformity of the color once inorganic materials are deposited in the pores (Figure 3). By not providing a final D.C. treatment to ensure uniformity of barrier film thickness, the resulting colored metallic substrate will often have a speckled appearance with rainbow-like patches interspersed throughout a colored background. Preferably, the duration of D.C. treatment is less than 20 minutes; shorter times resulting in a thinner barrier film 20 and a correspondingly shorter wavelength of light produced by optical interference. Use of a sequential treatment of direct and alternating current serves precisely to control the barrier film distance 20, thus enabling more control of the final colors when inorganic materials are deposited in the electrocoloring step (FIG. 3). The best results can be obtained by following a tripartite sequence as described above. Other combinations of direct and alternating currents can be used, provided that the alternating current is symmetrical. The final D.C. treatment can be eliminated, but the resulting color may not be uniform. In all embodiments of the improved modification steps described herein, the D.C. voltage is less than 20 volts. The alternating current is also less than 20 volts.

It is important to maintain a constant temperature with a variation of less than about 2-3° C during the modification process. A temperature of about 30° C or room temperature is preferred. At temperatures much higher than about 30° C, the anodic layer 16 is rapidly dissolved due to the higher chemical activity at the higher temperatures. The pores are then enlarged and more metal will be deposited in the subsequent electrocoloring step. This results in darker colors which may be less desirable under certain circumstances.

The time of each voltage treatment will depend on the temperature and other parameters but should be preferably less than 20 minutes, since at times beyond this point, the process becomes less efficient and consequently more expensive.

In a further embodiment of this modification step, special voltage characteristics are chosen to overcome the electrical resistance of the barrier film. As mentioned previously, the barrier film 20 is a semiconductor, and as the barrier film increases in size, the electrical resistance of the anodic layer 16 also increases concomitantly. Therefore, a preferred method of applying the direct current and symmetric alternating current is to apply the voltage in a linearly increasing manner, in other words, in a "ramped" configuration. This ramping may be particularly important during the A.C. treatment sequence, since the increasing resistance of the barrier film as the film enlarges tends to distort the symmetric sine wave input.

Another important feature of the invention is that these controlled direct and alternating current treatments can be performed in the anodizing bath (FIG. 1) as well as in the electrocoloring bath (FIG. 3).

Where the anodizing electrolyte is substantially free of metallic salts typically used in electrocoloring, such as metal salts, metallic deposits cannot form during the modification step. Where the anodic layer and barrier film are modified by the method of this invention in the electrocoloring bath itself, the electrolyte is not substantially free of metal salts and pigmentary deposits can form under alternating current conditions. Thus, when the improved modification step of this invention is performed in the electrocoloring bath, pore modification can commence simultaneously with formation of inorganic deposits. The specific voltage sequences described herein can, however, be employed to more precisely control the barrier film thickness and eliminate metal deposition prior to actual electrocoloring.

The alternating current voltage treatment of the modification step, which treatment would normally deposit unwanted metallic pigments in an electrocoloring bath, is chosen so that the extent of metallic deposition is kept to an absolute minimum. One way to accomplish this is to apply alternating current so as to provide for an extremely thin barrier film.

The final DC treatment of the modification step will cause slight redissolution of any metallic deposits that have been inadvertently formed during the alternating current treatment of the modification step in the electrocoloring bath. This step is advantageous because it provides a more precise control over the barrier film depth prior to actual electrocoloring, thus leading to more definition in the final color production when electrocoloring does take place under alternating current. When the modification step is performed in the electrocoloring bath, the procedure eliminates the need for separate modification and electrocoloring baths and more efficiently uses available chemicals and electrical equipment.

In yet another embodiment, the improved modification step can also be performed in a completely separate bath. This separate bath is typically an acidic electrolyte containing a carboxylic acid, sulphonated organic, or inorganic mineral acid, sulphuric acid, oxalic acid, or tartaric acid, etc.

Once the pores 18 and the height of the barrier film 20 are modified according to the improved process of this invention, inorganic materials are deposited in the thus-enlarged end region of the pores in the electrocoloring step (FIG. 3).

invention.

TABLE I

Film Heights (A)	Barrier film modification under DC or AC current (minutes)	Resulting Colors
400 to 415	2	grey
415 to 490	3	blue
490 to 560	4	green
560 to 580	5	yellow
580 to 660	6	red
660 to 700	8	purple

The second of the two anodized pieces was treated identically except that the three part modification step was eliminated. A bronze color was obtained.

EXAMPLE 2

This Example illustrates modification of the anodic layer in the electrocoloring bath using a dual sequence of direct current and sequence wave alternating current.

An aluminum piece was degreased in an alkaline cleaner and desmutted for 10 minutes in a 10% sodium hydroxide solution at 60° C. It was then rinsed, neutralized, and then anodized in a bath comprising 180 g/l sulphuric acid and 15 g/l aluminum sulphate at a temperature of 19 ± 0.5C and a direct current of 3 A/dm for 20 minutes with a positive charge. The electrodes were carbon.

The piece was rinsed and transferred to an electrocoloring bath containing 16 g/l stannous sulphate, 20 g/l nickel sulphate, 25 g/l sulphuric acid, 2 g/l phenosulphuric acid and 2 g/l citric acid. The aluminum piece as the positive pole was treated to a direct current of 0.4 A/dm for 3 minutes. Stainless steel electrodes were the negative pole. Next, the piece was subjected to a symmetrical square wave alternating current having a current density of 0.5 A/dm for 4 minutes and then to a symmetrical sinusoidal alternating current of 18 volts for 3 minutes. A green color was produced.

EXAMPLE 3

This Example illustrates modification of the anodic layer in the electrocoloring bath using a dual sequence of direct current and symmetrical alternating current.

A 6063 aluminum alloy piece was introduced into an anodizing bath having an electrolyte containing 155 g/l sulphuric acid, 3 g/l boric acid, 2 g/l glycerin, at a temperature of 24 ± 0.5C. Lead electrodes were used under pulsating direct current of 4 A/dm for 40 minutes. The piece was then transferred to a modifying bath and a direct current of 0.5 A/dm was applied for 5 minutes, the piece having a positive charge, in an electrolyte containing 200 g/l sulphuric acid. The piece was next treated by applying a symmetrical alternating current under current density of 0.8 A/dm for 2 minutes. Finally, the piece was rinsed and colored in an electrolyte containing 18 g/l stannous sulphate, 1 g/l ascorbic acid, 2 g/l citric acid with tin electrodes and subjected to alternating current at a voltage of 18 volts for 5 minutes until the desired color gray was obtained.

Even though the invention has been described and shown in connection with specific embodiments thereof, it is understood by those skilled in the art that modifications may be made to the invention itself or to any of its applications mentioned herein and that the same are encompassed within the spirit and scope of the invention, as defined in the following claims.

Claims

1. A process for the electrolytic coloring of a metallic substrate by optical interference effects, comprising:

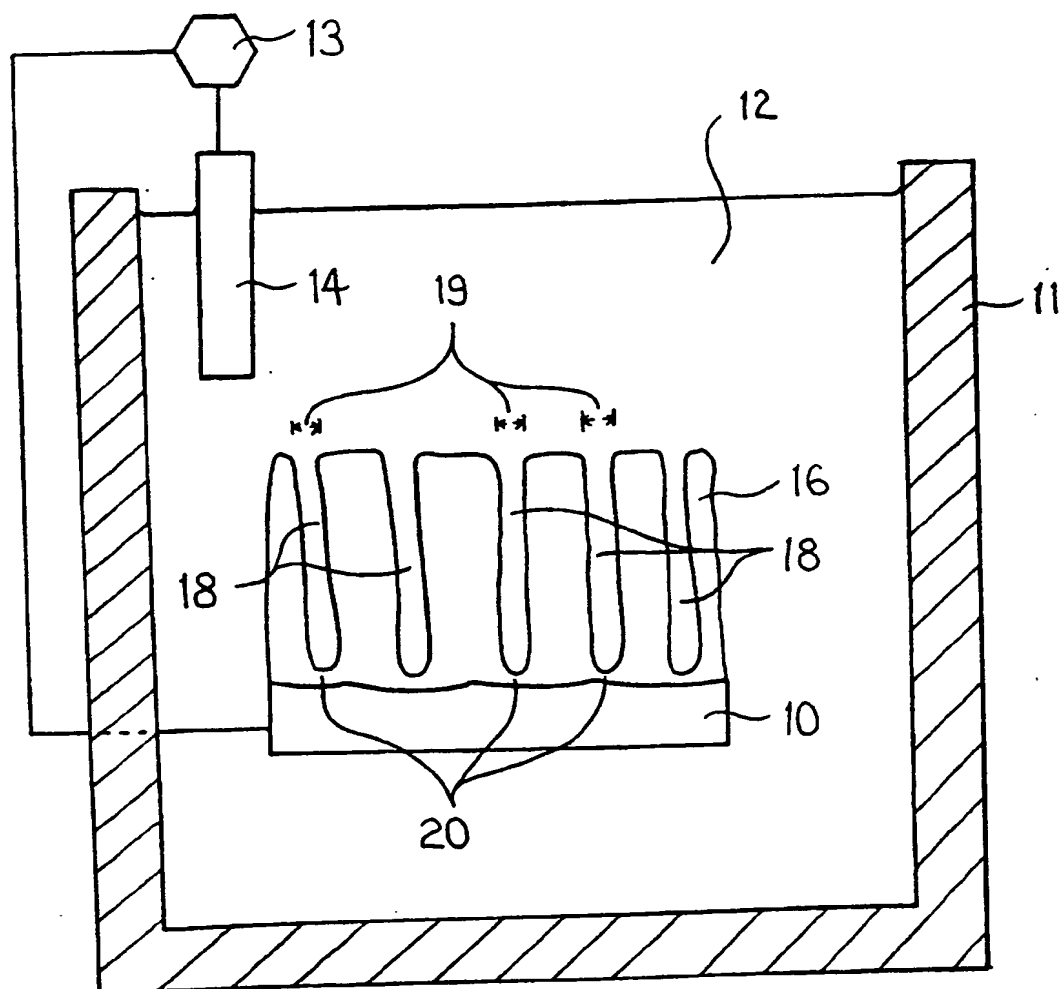


Fig. 1

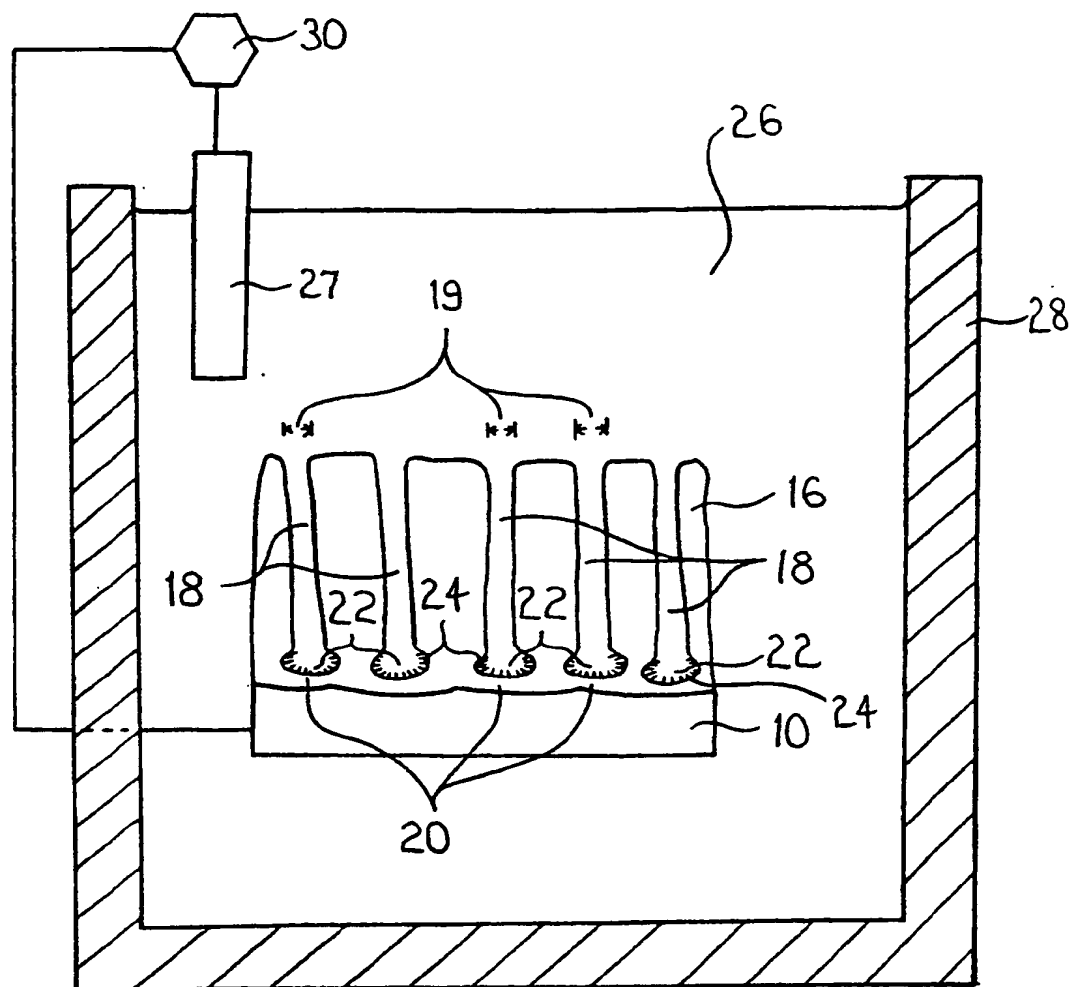


Fig. 3